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INVESTIGATION BY THE METHOD OF THERMOMECHANICAL CURVES OF THE THERMAL TRANSFORMATIONS OF CERTAIN RUBBERS

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The method of recording thermomechanical curves ([1]) offers broad possibilities for studying various processes that occur during the heating of polymeric materials. It proves especially convenient when automatic recording is used of the deformation of a specimen under the action of an applied force during a continuous and uniform rise in temperature. In this case it may be placed alongside such a widespread method of investigation as thermography, whose applicability to polymers, incidentally, is quite limited.

For the study of rubbers, the method of thermomechanical curves has, in our opinion, been used insufficiently. A. A. Tager and co-workers ([2]) showed the effectiveness of applying this method to the study of processes occurring during the heating of synthetic sodium-butadiene rubber. The curves obtained by Kargin' s balance method with periodic application of load ([3]) pass through a maximum corresponding to the greatest fluidity of the polymer. The authors associate the decrease in fluidity at higher temperatures with the formation of bridge bonds and spatial networks.

We set ourselves the task of investigating the processes occurring during the heating of rubbers by constructing thermomechanical curves using the technique of applying a constant load while uniformly raising the temperature of the specimen ([4]).

Improvement of the technique made it possible to carry out automatic recording of the curves, directly in the temperature–deformation* coordinates ([5]).

Recording is carried out on an EPP-09 electronic potentiometer. Along one of the coordinates, set by the pen of the recorder, the emf of a thermocouple determining the temperature of the specimen under study is registered. The second coordinate is set by the movement of the chart tape, which is carried out not continuously but as the material under investigation is deformed. The punch pressing on the specimen is connected with the contact sensor of an

Fig. 1. Natural rubber smoked sheet. 1 —unchanged specimen; 2 —specimen thermostated at −25° for 1.5 hours; 3 —the same for 3 hours; 4 —specimen preheated to 250°

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electronic relay, which switches on the motor of the tape-drive mechanism of the potentiometer. (In this case, depending on the direction of deformation, the motor receives direct or reverse rotation.) The same mechanism drives a micrometer screw that "follows" the contact moving as the punch penetrates into the specimen. Rubber specimens were cut out in the form of a tablet 4 mm in diameter and 2 mm high. The end of the punch transmitting pressure to the specimen had a flat cut; its diameter was 2.0 mm. Heating of the specimens was carried out according to a linear program within the range from −120 to +450°. A stream of dry nitrogen brought to the temperature of the block was continuously introduced into the block, thereby achieving better heat transfer to the specimen and reducing the possibility of its oxidative destruction.

* Strictly speaking, what is studied is not the deformation of the specimen, but penetration, and the method should be called thermopenetrographic.

The heating rate in all experiments was 2 deg/min, the load 3.2 kg/cm^2. In a number of cases other loads were also used. All thermomechanical curves of rubbers obtained by us have been reduced to a single scale along the deformation axis (for which a special simple device based on the method of optical projection was used). Deformation is given in relative percent.

As is known, for amorphous polymers of sufficiently high molecular weight the thermomechanical curves are characterized by the presence of regions corresponding to the glassy, highly elastic, and viscous-flow states, as well as transition sections between them. The region of high-elastic deformation on the curve corresponds to a horizontal plateau which, however, often has an upward slope owing to the accompanying plastic deformation of the polymer.

On the thermomechanical curves of natural rubber (Fig. 1, 1) an additional "step" is found in the region of the high-elastic state. This element of the curve is quite reproducible. We observed it on curves of specimens taken from various sources, subjected to storage for different durations and under different conditions. It should be noted that in earlier studies of thermomechanical properties by constructing curves point by point ([6]), this feature of NR was not detected.

Fig. 1. Natural rubber smoked sheet. 1 —unchanged specimen; 2 —specimen thermostated at −25° for 1.5 hours; 3 —the same for 3 hours; 4 —specimen preheated to 250°.

We succeeded in showing that the appearance of the "step" is connected with

Fig. 2. Synthetic rubbers obtained on chelate catalysts: butadiene SKB (1), SKV (2), SKBM (3), and piperylene SKP (4)

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the process of melting of the crystalline phase of rubber, which takes place near 0°C. Since, according to literature data ([7]), the optimum temperature for crystallization of rubber is −25°, we thermostated a rubber specimen at this temperature for 1.5 or 3 hours, then cooled it below the glass point, after which the thermomechanical curve was recorded in the usual manner. It turned out that the form of the curve depends on the duration of thermostating of the specimen at the temperature of optimum crystallization. The ratio of the heights of the first and second plateaus decreases with increasing holding time (Fig. 1, 2, 3). This leads to the assertion that the second plateau owes its origin to melting of the crystalline phase. It is characteristic that none of the synthetic rubbers studied, including isoprene SKI, exhibits such a phenomenon.

Fig. 2. Synthetic rubbers obtained on chelate catalysts: butadiene SKB (1), SKV (2), SKBM (3), and piperylene SKP (4).

Each of the synthetic rubbers studied is distinguished by a quite definite glass point T_g (this temperature, at different values of the applied load, coincides within the limits of experimental accuracy). The curves of a number of synthetic rubbers (Fig. 2) are of the same type, and the differences are apparently determined mainly by the magnitude of the molecular weight.

On all the curves at the point T_g there is a sharp rise, but there is no clearly expressed horizontal plateau, which indicates that already

beginning at the transition temperature, the elastic deformation of the rubber is accompanied by plastic deformation.

The curves for one of the samples of butadiene rubber obtained on a lithium catalyst, SKLD, of very low plasticity differ substantially from the others. Following an increase in deformation, at about 200° a horizontal plateau appears, lasting up to very high temperatures. Only above 400° does the sample melt (Fig. 3A). Another SKLD sample of higher plasticity gave a thermomechanical curve whose shape did not differ from the curves of other synthetic rubbers (B in the same figure).

It was natural to suppose that the peculiar course of the curves for the first SKLD sample is explained by the fact that, owing to its low plasticity, penetration is not completed at temperatures at which the polymer is stable. In view of this, the experiment continues in the temperature range where destruction occurs and, after it, crosslinking of the polymer into a rigid structure that melts at a very high temperature (thermovulcanization). To verify the correctness of these considerations, the SKLD sample was subjected to preliminary heating

Fig. 3. Synthetic rubber SKLD (butadiene, polymerized in the gas phase on a lithium catalyst). A—low plasticity, B—high plasticity; 1—samples heated to 250°, 2—sample heated to 150°, 3—plasticized on rolls

Figure 3: Fig. 3. Synthetic rubber SKLD (butadiene, polymerized in the gas phase on a lithium catalyst). A—low plasticity, B—high plasticity; 1—samples heated to 250°, 2—sample heated to 150°, 3—plasticized on rolls

to 250° under the conditions of the usual experiment (but without application of the load), after which it was cooled. Then the thermomechanical curve of this preheated sample was recorded. It turned out that, despite preservation of the value of the glass-transition point T_g, the sample had acquired entirely different elastic-plastic properties (curve A-1). The heated sample shows an absence of plastic deformations up to temperatures of about 400°. (The reverse course of the deformation in the temperature range 100-300° is apparently due to a change in the volume and elastic properties of the materials, which may be connected with the regime of its cooling after heating.) This experiment clearly shows that when the SKLD sample is heated to 250° it is transformed into a rigid, high-melting material.

Fig. 3. Synthetic rubber SKLD (butadiene, polymerized in the gas phase on a lithium catalyst). A—low plasticity, B—high plasticity; 1—samples heated to 250°, 2—sample heated to 150°, 3—plasticized on rolls.

It was natural to suppose that the SKLD sample having high plasticity should also possess this property. We heated sample B to a temperature of 250° (lying beyond its penetration by a load of 3.2 kg/cm^2, i.e., in the region of the fluid state), and after cooling recorded the thermomechanical curve. In this case curve B-1 was obtained, almost no different from that given under analogous conditions by the sample of lower plasticity (A-1). It is noteworthy that nothing similar was shown by rubber heated to 150° (B-2). The curve in this case lies somewhat to the left of that for the original polymer. This indicates that there has been some decrease in molecular weight, i.e., degradation, but by no means structuring. Still farther to the left in the graph lies the curve of a sample of the same material previously subjected to thermoplasticization on rolls with the use of minimal amounts of chemical plasticizers (B-3).

The result obtained made it possible to suggest that structuring at high temperatures can also be detected on thermopenetration curves of other synthetic rubbers when they are heated, already in the fluid state, to 250°.

In an experiment carried out with a sample of ordinary SKB, these assumptions were confirmed. The corresponding curves are similar to those found for SKDD and are not given here. It is curious that a sample of stereoregular butadiene rubber SKD, obtained by synthesis with a complex catalyst, also showed, in general, the very same picture (Fig. 4). Heating in this case as well led to the formation of a hard, high-melting product. It was of interest to investigate

Fig. 4. Synthetic rubbers obtained with a complex catalyst. A—Butadiene SKD, B—isoprene SKI. 1—samples preheated to 250°

Figure 4: Fig. 4. Synthetic rubbers obtained with a complex catalyst. A—Butadiene SKD, B—isoprene SKI. 1—samples preheated to 250°

the behavior of NR under analogous conditions. A sample of NR was heated, like the previously mentioned samples, to 250°. The thermopenetration curve recorded after its cooling is shown in Fig. 1, 4, where the curves of unchanged NR are also shown. As is evident from their comparison, heating the rubber leads to the formation of a more plastic product, flowing at room temperature. This indicates that degradation has occurred, not accompanied by the formation of rigid structures. Synthetic isoprene rubber SKI behaves, in this respect, quite analogously to natural rubber. The curves obtained by us (they are shown in Fig. 4) indicate that degradation also occurs in this rubber, but the formation of rigid, high-melting structures is not observed.

Fig. 4. Synthetic rubbers obtained with a complex catalyst. *A* —butadiene SKD, *B* —isoprene SKI. *1* —samples preheated to 250°.

It is noteworthy that synthetic piperylene rubber SKP behaves like isoprene rubber, and not like butadiene rubber. We do not present the curves obtained here. As a result, it appears possible to distinguish readily between butadiene rubbers (regardless of the methods of their synthesis) and methyl-butadiene rubbers (natural or synthetic) by heating to 250° and subsequently recording the thermomechanical curves.

Thus, as a result of the work carried out, it has been shown that the study of thermomechanical properties using an automatic recording apparatus is an effective method for investigating rubbers. Thermomechanical curves have been obtained for natural rubber and for a number of synthetic rubbers, and the processes of their thermal transformations have been investigated. It has been shown that butadiene rubbers, when heated to 250°, form rigid "crosslinked" structures, whereas pentadiene rubbers under these conditions undergo degradation. The crystallization process of natural rubber has been investigated, and the temperature range of melting of the crystalline phase has been identified.

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Note: Figure translations are in progress. See original paper for figures.